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MICROSTRUCTURAL FORMATION AND EFFECTS ON THE PERFORMANCE OF PLATINUM MODIFIED ALUMINIDE COATINGS

by

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The use of noble metal modified aluminide coatings has gained renewed interest as the requirements of improved protectivity for gas turbine engine components has increased. Increasing temperature, severity of operating environment and required lifetime extension are cited as reasons for their selection. While the literature documents examples of significant improvements in hot corrosion resistance at low (800° C) and high (800° C) temperatures and in cyclic oxidation with Pt additions, there are also examples of limited improvements and even detrimental effects. These controversies have been preliminarily

ascribed to the considerable differences in microstructural features possible in these systems and to the variation in test procedures between laboratories, and between rigs and engines. A systematic study was therefore initiated to identify the microstructural variations obtained for platinum-modified aluminide coatins on IN738 and to develop a fundamental understanding of their mechanism of formation. In this final report, the several classical structural types are defined together with the beginnings of their formation understanding. These microstructures were then subjects to a series of tests under conditions including hot corrosion at 700 and 900° C, and cyclic oxidation. In addition, measurements of mechanical properties such as DBTT were performed.

It was found that platinum addition to a standard aluminide is beneficial at 900° C, so far as hot corrosion attack is concerned. Hot corrosion resistance at 700° C is strongly structure dependent with most structural types offering little advantage over the unmodified aluminides. Pre-aluminizing heat treatments and their resulting effect on the coating structure and composition are important factors that seem to be the dominant controlling factor for the tensile ductility and corrosion resistance. The resulting surface roughness of these coatings and the selective interaction of the Pt with specific substrate elements may play an important role in the ultimate behavior of these coatings and their performance in cyclic oxidation.

TABLE OF CONTENTS

		PAGE NO.
FORWARD		(ii)
ABSTRACT		(iv)
I.	INTRODUCTION	1
II.	BACKGROUND	3
	A. THE AVAILABLE PLATINUM ALUMINIDE COATINGS	3
	B. PRESENT STATE OF KNOWLEDGE ON HIGH TEMPERATURE CORROSION AND OXIDATION BEHAVIOR	4
III.	PRESENT STATUS OF PLATINUM MODIFIED ALUMINIDE COATINGS UNDERSTANDING	10
	A. STRUCTURE AND FORMATION MECHANISMS OF PLATINUM.MODIFIED ALUMINIDE COATINGS	10
	B. HOT CORROSION	19
	C. CYCLIC OXIDATION	22
	D. MECHANICAL PROPERTIES	24
	E. CONCLUSIONS	26
LIST OF REFERENCES		28
ACKNOWLEDGEMENT		31
APPENDIX I		32
APPENDIX II		33
APPENDIX III		39

LIST OF TABLES

I. Pre-aluminizing diffusion heat treatments evaluated

II. X-ray analysis results of Pt modified aluminide coatings

LIST OF FIGURES

Figure 1. Typical inward type Pt-Al structures exhibit effect of pre-aluminizing heat treatments: (a) 1/2 hr. at 870° C, (b) 2 hrs. at 980° C, and (c) 1 hr. at 1050° C.

Figure 2. SEM photomicrograph of inward type Pt-Al structure contains four zones.

Figure 3. Typical outward type Pt-Al structures exhibit effect of pre-aluminizing heat treatments: (a) 1/2 hr. at 870° C, (b) 3 hrs. at 1040° C, and (c) 4 hrs. at 1080° C.

Figure 4. The outer-zone structure of Pt-Al coatings exhibit: (a) single phase, inward type structure and (b) two phase outward type structure.

Figure 5. Effect of prolonged exposure of Pt-Al coatings in air at 1080° C exhibit: (a) single phase structure after 1 hr. heat treatment and (b) single phase structure after 24 hrs. heat treatment.

Figure 6. Effect of prolonged exposure of outward type Pt-Al coatings in air at 1080° C exhibit: (a) two phase structure after 1 hr. heat treatment and (b) single phase structure after 24 hours heat treatment.

Figure 7. Elemental distribution across the Pt-Al coatings: (a) Pre-aluminizing heat treatment, 1/2 hr. at 870° C, (b) Inward type coating and (c) outward type coating.

Figure 8. Possible modification of NiAl diffusion data (29) with the addition of Pt.

Figure 9. Surface attack of Pt modified aluminide coatings exposed for 200 hours hot corrosion condition at 900° C with various pre-aluminizing diffusion heat treatments.

Figure 10. Typical low temperature hot corrosion attack at 700° C: (a) specimen exhibits little attack on $PtAl_2$ phase and (b) substantial hot corrosion attack beneath the $PtAl_2$ phase.

Figure 11. SEM photomicrographs exhibit: (a) inward type LTHA platinum-aluminide coating and (b) typical LTHC attack after 100 hours exposure at 700° C.

Figure 12. Typical example of surface rumpling of Pt-Al coatings: (a) sample exhibits macro surface roughness (8x), (b) enlarged photomicrograph (64x) and (c) cross-section of same specimen showing surface upheaval on the order of 50 μm.

Figure 13. Ductile to brittle transition temperature (DBTT) and fracture strain of Pt-Al coatings as function of structure and Al-Pt content.

FORWARD

Research presented in this report is the result of an Office of Naval Research sponsored program begun in 1981. This effort was jointly funded at the Lawrence Berkeley Laboratory, University of California and the Department of Mechanical Engineering, Naval Postgraduate School through FY84 and completed at the Naval Postgraduate School through FY85. During this program, a number of scientists and students participated in various phases of the research. They are listed in Appendix I. A summary of the publications and presentations from this work are listed in Appendix II. Ongoing research programs and activities initiated during this effort are listed in Appendix III.

ABSTRACT

The use of noble metal modified aluminide coatings has gained renewed interest as the requirements of improved protectivity for gas turbine engine components has increased. Increasing temperature, severity of operating environment and required lifetime extension are cited as reasons for their selection. While the literature documents examples of significant improvements in hot corrosion resistance at low (<800° C) and high (>800° C) temperatures and in cyclic oxidation with Pt additions, there are also examples of limited improvements and even detrimental effects. These controversies have been preliminarily ascribed to the considerable differences in microstructural features possible in these systems and to the variation in test procedures between laboratories, and between rigs and engines. A systematic study was therefore initiated to identify the microstructural variations obtained for platinum-modified aluminide coatings on IN738 and to develop a fundamental understanding of their mechanism of formation. In this final report, the several classical structural types are defined together with the beginnings of their formation understanding. These microstructures were then subjected to a series of tests under conditions including hot corrosion at 700 and 900° C, and cyclic oxidation. In addition, measurements of mechanical properties such as DBTT were performed.

It was found that platinum addition to a standard aluminide is beneficial at 900° C, so far as hot corrosion attack is concerned. Hot corrosion resistance at 700° C is strongly structure dependent with most structural types offering little advantage over the unmodified aluminides. Pre-aluminizing heat treatments and their resulting effect

on the coating structure and composition are important variables that seem to be the dominant controlling factors for the tensile ductility and corrosion resistance. The resulting surface roughness of these coatings and the selective interaction of the Pt with specific substrate elements may play an important role in the ultimate behavior of these coatings and their performance in cyclic oxidation.

I. INTRODUCTION

The development of new generation, higher performance, and cost-effective heavy duty gas turbine engines demands longer service life as compared to the engines used in the early seventies. These engine components made of superalloys, are generally exposed to very high operating temperatures in conjunction with a wide variety of lower grade fuels, and often are used in marine environments. Therefore, high temperature hot corrosion and oxidation are common failures modes of these turbine engine components and/or other fuel fired energy systems.

Diffusion aluminide coatings (1,3), commonly deposited by the pack cementation process, were first applied on superalloy substrates to improve high temperature oxidation and hot corrosion resistance and thus improve the service life of gas turbine engines and their components. It has been reported that the simple or unmodified aluminides suffer hot corrosion attack caused by the fluxing of the protective scale by molten salts and the impurities present in the combustion gases (4). Besides this, the protectivity and durability of the simple aluminide coatings depend to a major extent on the substrate alloys composition. This prompted the development of the MCrAlY class of overlay type coatings designed to provide a protection system essentially independent of the substrate and with a variable composition optimized to provide hot corrosion resistance and in some instances improved mechanical properties such as ductility and thermal fatigue resistance. The MCrAlY overlay coatings are generally produced by electron beam physical vapor deposition (EB-PVD) or advanced plasma spray techniques (5,6).

The aluminide coatings, modified by the additions of critical alloying elements, have gained renewed interest because they offer economical alternatives to the EB-PVD and plasma spray deposition techniques. A number of alloying elements have been tried to improve the coatings, including chrominum, silicon, and the "active elements" like hafnium and, finally, the noble metals such as platinum (7,8).

Aluminide coatings modified by the additions of platinum, rhodium and palladium have been known for a number of years and used in production applications for the protection of airfoils in heavy duty gas turbine engines and various other aircraft and marine engines. However, there have been some controversies on the advantages of, and the reason for, the beneficial effects of platinum in the modified aluminide coatings corrosion and oxidation resistance (9-24). It has been suggested that these conflicting findings are mainly the results of differences in the structures reported for the various types of coatings investigated. Few data are available in the literature on the mechanical behavior of these systems.

In recent years there has been a renewed interest in the possible performance and economic benefits to be gained from the use of the platinum aluminide coatings. It is also seen in the literature that there has been an increase in research activity into the platinum modified aluminide coatings. The objective of this final report is to review the present state of knowledge in this area together with the latest test results developed in this program to provide a better understanding about these unique surface structures and their performance under hostile environments.

II. BACKGROUND

A. THE AVAILABLE Pt-ALUMINIDE COATINGS

In a review of the structures of "standard" Pt-Al structures (1-27), it was apparent that a wide range of variations were possible for the available commercial and developmental coatings, and that the existance of such differences might help to explain some of the apparent test anomalies reported. The first commercial Pt-Al system was produced by Lehnert, et al. (7) and designated LDC-2 with a reported four-fold life increase in cyclic oxidation and a greater than two-fold improvement in hot corrosion resistance over a simple unmodified aluminide coating. The structure of the LDC-2 coating was found to have a single phase $PtAl_2$ surface structure containing some Ni. It was later learned that Cape (8) and others (9) had earlier disclosed the possible beneficial effects of Pt additions to coating systems.

A second coating structure described by Seelig, et al. (10), and designated RT-22, though formed by the same process, i.e., initial Pt electrodeposition followed by pack aluminizing, exhibited a two-phase structure. In comparison with the LDC-2 version, a more uniform, deeper gradient of a lower concentration of Pt dissolved in the cubic β(Ni,Al) phase is present in the RT-22 together with a dispersion of a $PtAl_2$ second phase. In this coating system as well as others, the density and distribution of this second phase appears to vary in a number of the samples examined and is hence a fruitful area for research.

A potential third version (although not necessarily a different type) of Pt-aluminide structure developed at Johnson Mathey in collaboration

with Rolls-Royce, designated JML-1, was perfected and described by Wing and McGill (11). A fused salt platinum electrodeposition technique was used followed by a high activity aluminizing treatment. This coating is reported to have a different structure and platinum distribution with the presence of a thick Pt_2Al_3 outer layer over a duplex $(Ni,Pt)_2\ Al_3$ + PtAl structured zone. The apparent absence of $PtAl_2$, the Pt-rich phase reported in many Pt-aluminide coatings, is not explained. (Note that this Pt_2Al_3 phase has not been reported in other studies, and a subsequent paper identified the phase as $PtAl_2$).

It was apparent from these and other observations that a range of possible Pt-aluminide structures could be produced within a fairly standard envelope of coating processing parameters. (Unfortunately, in most of the earlier studies, little information on actual processing parameters or the resulting structures was provided). The possible variables included amount (thickness) and deposition mode of the initial Pt layer, the possibility of pre-aluminizing diffusion of the platinum with the substrate, the aluminizing cycle at activities varying from high to low, followed by post aluminizing coating diffusion and substrate solution heat treatments at varying temperatures for varying times.

B. PRESENT STATE OF KNOWLEDGE ON HIGH TEMPERATURE CORROSION AND OXIDATION BEHAVIOR

A variety of results have been reported on the hot corrosion and oxidation resistance of platinum modified aluminide coatings. The major conclusion of these studies are discussed in this section. In a comparative investigation on a series of aluminides containing noble metals, i.e., Pt-aluminide and Pt-Rh-aluminide, on two cobalt-base superalloys X-40 and MAR-M-509, tested along with a standard aluminide

and a CoCrAlY coating in a low-velocity atmospheric-pressure burner rig, R. M. Clarke (12) has shown that in high temperature 900° C hot corrosion conditions, the Pt-aluminide was the most corrosion-resistant aluminide coating tested. It performed almost as well as the CoCrAlY composition specially designed to resist high temperature hot corrosion. The ranking of the tested coatings after 500 hours of attack indicated an increase in corrosion resistance from the modified aluminides to Pd, Pt-Rh, and Pt-aluminide coatings. The Pt-aluminide exhibits half as much oxide penetration as the standard aluminide. However, in low temperature (704° C) hot corrosion tests, the Pt-aluminide was found to be only slightly more resistant than the simple aluminide and performed more advantageously than CoCrAlY, while in high temperature burner-rig tests the Pt-aluminide on MAR-M-509 and the CoCrAlY coating had nearly identical corrosion rates. Both a structural effect and a substrate effect were observed for these Pt-aluminide coatings. The two-phase RT-22* coating on MAR-M-509 appeared to have slightly better hot corrosion resistance, in both temperature ranges, than a single CODEP B2 + Pt (experimental coating structure attempted for this study) on the X-40 substrate.

Bauer, Schneider and Grunling (13) confirmed the improvement with Pt additions for two common Pt-aluminide coatings, RT-22 and LDC-2 in a laboratory hot corrosion crucible test as well as in engine service operation. In the tests Bauer et al. found that, at the 850° C intermediate temperature, both Pt-aluminide coatings were able to prevent

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*It should be noted here and elsewhere that distinctions between coating types should not be made on the simple basis of the letter designation (i.e., LDC-2, RT22, etc.) but rather on the specific coating structure and Pt content of the specimens tested. Unfortunately in many studies this information is not provided.

IN 738 base material corrosion attack for periods of about 1000 hours while an unmodified aluminide of similar thickness was degraded in less than 500 hours. Microstructural analyses revealed that one Pt-Al coating suffered extensive internal corrosion of the NiAl layer near the interdiffusion zone. This attack could be considered to be the predominant failure mechanism. In engine service testing on first stage blades, more pronounced internal attack of one structure than the other also occurred. At the higher termperature, 950° C, less severe corrosion conditions exist where the SO_3 partial pressure drops to a level where acidic fluxing becomes negligible compared to the rate of oxidation and the protection lifetime of the Pt-aluminide increases dramatically. The protection mechanism seems to be based on the formation of adherent scales and possibly the form and distribution of the Pt in the NiAl layer in juxtaposition. No more corrosion attack occurs and the LDC-2 coatings become much more protective providing twice as long a penetration life as RT-22.

A similar result is reported by Hanna, et al. (14) for the 1000° C oxidation of a series of Pt-aluminized IN 738 samples with various structures obtained by aluminization of electroplated platinum of various thickness. They observed that the initial oxidation rate (i.e., weight gain) for any of the Pt-aluminide coatings was more than one order of magnitude slower than for the unmodified aluminide, and that the performance of the (Ni,Pt)Al single-phase coating, i.e., the homolog of the LDC-2, was slightly superior to the other platinum-aluminides.

The JML-1 coating, tested for a 500-hour period by Wing and McGill (11) on the two MAR-M-002 and IN 738 alloys in burner rig cyclic conditions shows apparent outstanding performance, slightly better for

the 850° C intermediate temperature than for the 750° C low temperature hot corrosion attack. A comparison with a JML-2 system (a modification of JML-1 with a different platinum distribution provides fair protection at the higher temperatures but has an even greater limitation for low temperature hot corrosion) enabled them to conclude that the single phase $PtAl_2$ layer system JML-1 is a better corrosion resistant coating.

Chigasaki, et al. (15) have reported that in burner rig testing at 850° C and below, in sulfur bearing fuel, the hot corrosion resistance of a two zone aluminide coating structure (i.e., outer layer is a high Al NiAl and the inner layer consists mainly of low Al NiAl), can be improved. This is accomplished by increasing the thickness of the outer layer of the coating to >80 μm. This system then becomes even more resistant than the platinum aluminide coatings where they found preferential attack of the $PtAl_2$ phase dispersed in the outer layer of the modified coating. Preferential attack of $PtAl_2$ in a two phase structure has also been reported by Bauer, et al. (13), as previously noted.

In a study of the composition and morphology of platinum aluminide coatings produced by one aluminizing process, Jackson & Rairden (16) have found that the morphology of the resulting coating is highly dependent upon the thickness of the platinum pre-deposit. With thick platinum layers, the refractory metals from the substrate alloy are excluded from the outer surface of the coating. Herein may reside, at least in part, the reason of the improvement of hot corrosion resistance of superalloys when protected by platinum aluminide coatings. If potential deleterious elements from the alloy, such as Mo, W, Ti, etc. are "buried" beneath or somehow tied up near the substrate interface, they cannot contribute to accelerated hot corrosion at the surface.

In electrochemical measurements of a platinum modified (designated LDC-2) and a platinum-free aluminide coating in a $(Na, K)_2SO_4$ melt at 900° C, Rahmel (17) observed that the Pt-rich surface layer exhibits a broader passive range than the Pt-free surface. The Pt-free coating corrodes significantly faster in the passive range. The resistance to acidic fluxing is similar for both coating types, but the Pt-rich surface has a significantly higher resistance to basic fluxing. Finally, in an earlier investigation and later rerun as part of a study of Cr effects, Boone, et al. (18) found little difference between any of the commercial structural variation of platinum-aluminide coatings in furnace hot corrosion testing in the low temperature range.

This survey of the present understanding of the corrosion behavior of platinum modified aluminide coatings reveals that the performance of these systems is strongly dependent on structure and composition. In these studies there is some controversy about the optimum Pt level required for these coatings, with 40-60% often being mentioned. When a $PtAl_2$ phase is sampled, clearly a "high" Pt level is reported. However, volume fraction of $PtAl_2$ and the composition of the matrix NiAl phase may be even more critical in the resulting protectivity such that reliance on Pt level alone may not be sufficient. Because these structures vary with the source and the production time frame (21), it is not possible today to have a clear view on critical factors affecting protectiveness of these systems in the various hot corrosion conditions.

For these reasons studies by Boone, et al. (18-21) were initiated under Office of Naval Research sponsorship aimed at defining the relationship between the platinum modified aluminide coating structure and their protective properties. A preliminary investigation (19) of the

thermal stability by heat treatment in air at 1080° C of a series of Pt-aluminide coatings from two commercial sources, i.e., with the two archetype structures, (1) single phase $PtAl_2$ and (2) two-phase has pointed out that the oxidation resistance may also be markedly dependent on the structure. A sequence of specific structures of the "A" series of the platinum modified coatings, which will be outlined below, related to the processing parameters, i.e., the platinum deposition treatment and the aluminizing conditions, has been established (19). This series of structural types were evaluated in furnace hot corrosion tests under both low temperature acidic fluxing conditions at 700° C, and high temperature basic fluxing conditions at 900° C (20). Results are reported in the following sections.

III. PRESENT STATUS OF PLATINUM MODIFIED ALUMINIDE COATINGS UNDERSTANDING

A. STRUCTURE AND FORMATION MECHANISMS OF PLATINUM MODIFIED ALUMINIDE COATINGS

The structure and formation mechanisms of diffusion aluminide coatings are well understood (1,2). However, their performance under harsh environments, i.e., especially under hot corrosion, is limited and they are highly substrate composition dependent. As mentioned earlier, the addition of noble metals such as platinum to the aluminide coatings may be beneficial under hot corrosion and oxidation environments. It is reported that the addition of Pt to the aluminide coatings improves hot corrosion resistance at high temperature but that it is not as beneficial at lower temperatures. In the following paragraphs, the structure and formation mechanisms of Pt modified aluminide coatings as they are presently understood are discussed in greater detail. It should be noted that during the course of this research, significant progress has been made in the development of the understanding of these mechanisms. However, additional research is needed particularly in the areas of phase diagrams and diffusional mechanisms and is in progress.

Several application techniques are commercially available for the deposition of Pt on superalloy substrates (22). They include (i) electroplating, (ii) ion plating, and (iii) sputtering. Of these application techniques, the electro-deposition technique (i.e., electroplating) is the most commonly used for the production of Pt-Al coatings. The amount of Pt deposition can be varied, but in these studies, was kept constant at 8-10 μm. It is known that these process variables can produce different surface structures, but at present, there is no indication of any benefit of one over the other except in the

possible area of cost. In these studies to be reported here, the electroplated specimens* are given a selective pre-aluminizing diffusion heat tratement as listed in Table I. Pre-aluminizing diffusion heat treatments facilitate Pt diffusion and thus change the surface Pt content which result in selective interaction with substrate elements. The heat treated specimens are then aluminized by pack cementation and vapor phase processes (20,23). Two aluminizing conditions (1) high activity, aluminum rich packs at low temperatures (about 700-900° C) known as LTHA and (2) low activity, lean aluminum packs at high temperatures (1000-1100° C) known as HTLA are generally used for the deposition of aluminum on the pre-diffused platinum enriched layer. These aluminizing conditions control the as-deposited aluminum level, surface phase structure and hence, the nature of diffusion processes occurring in the Pt enriched layer. A complete understanding of the effect of Pt level on Al and Ni diffusion processes in high Pt alloys is not known but some preliminary thoughts will be presented separately. The amount of Al deposited is mainly controlled by time in the aluminizing process. Preliminary studies however, revealed that the presence of Pt increases the rate of Al pick up over the unmodified aluminide coatings for both types of aluminizing processes (24).

In a manner similar to the processes found for the diffusion aluminide coatings, two major types of structures, i.e., (1) inward and (2) outward can also be defined for the Pt modified aluminide coatings. Inward type Pt-Al coatings are formed by aluminizing pre-diffused

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*All data reported herein are based on IN-738 superalloy.

electroplated platinized layer in LTHA packs+. The aluminum diffuses through the pre-diffused Pt enriched surface layer and thus results in a high aluminum gradient across the Ni-Al coating. After the aluminizing treatment, the specimens are given a further heat treatment referred to as the post-aluminizing heat treatment which is mandatory for the Pt-Al coatings produced by the LTHA process and for many substrates as well.

The magnitude of the Pt level and the extent of diffusion distance are strongly dependent on the pre-aluminizing diffusion heat treatments. A very high level of Pt in a limited zone near the surface can be achieved with a minimum pre-aluminizing diffusion treatment. This high level of Pt near the surface interacts with the incoming aluminum atoms during the aluminizing process and thus produces a thin continuous single phase layer. Streiff, et al. (20) have identified this single phase layer as $PtAl_2$. However, there is some ambiguity regarding the identification of this single phase structure (11). Throughout this report, this continuous single phase structure will be designated as $PtAl_2$. In these studies it became very apparent that the aluminum activity level in the coating process was extremely critical in controlling the final structure of the coatings. Unfortunately, it was not always possible to control this variable to the degree required such that some coating structural variability was seen even for samples produced under the so-called "same condition".

+ While designated here as an Inward Type, selective Al diffusion through the pure Pt has not yet been clearly established. However, once aluminum penetrates through the Pt-enriched zone, the coating is of sufficient aluminum content (i.e., hyperstoichiometric β NiAl) to result in inward aluminum diffusion.

Figure 1 illustrates the typical optical photomicrographs of an inward Pt-Al coating with various pre-aluminizing diffusion heat treatments. The inward type Pt-Al coating exhibits the four zone structure shown in Figure 1(a). The surface zone consists of a high platinum content single phase $PtAl_2$. It should also be noted that random grit blast particles are also present at the interface of the initial substrate surface and the Pt over layer. These particles act as an excellent marker for the identification of subsequent diffusion processes. The outer intermediate zone can consist of either fine platinum-rich precipitates in an NiAl* matrix enriched in Al or an Al-rich NiAl precipitate in continuous $PtAl_2$ phase. The matrix and morphology of these precipitates depend on several factors including the Al activity level during the aluminizing treatment and possibly the structure of the platinum interdiffusion layer. The inner intermediate zone is a single phase NiAl (Ni-rich) denuded of any other phases or substrate elements. The innermost zone is the so-called interdiffusion zone which consists of substrate phases and elements insoluble in β(NiAl) which formed when Ni was withdrawn by the Al-rich surface as previously established for simple aluminides. Any Pt pre-diffused into these outer zones would be expected to be precipitated as $PtAl_2$ (at sufficiently high Al levels as discussed below).

Figures 1(b) and 1(c) exhibit the typical three zone structure. The outer zone is platinum rich $PtAl_2$ phase in an NiAl matrix rich in Al; while the intermediate zone is a single NiAl phase and the innermost zone

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*There is some indication of two types of NiAl phase structure (20). Besides this, a variety of single phase NiAl structures can be formed by varying the relative amount of Ni and Al.

is the so-called interdiffusion zone. Streiff, et al. (20) have reported the structural changes of Pt-Al coatings produced by the LTHA process, as determined by x-ray diffraction study. The x-ray data of Pt-Al coatings are listed in Table II. It is interesting to note that the surface structure changes from single phase to two phase and then followed by a single phase β(NiAl) with prolonged pre-aluminizing heat treatments. When these specimens were examined under the Scanning Electron Microscope (SEM), it was found that much better microstructural detail was obtained than with optical metallography. This could be the result of two factors; (1) resolution limitation (i.e., optical microscope) and (2) polishing problem with very brittle surfaces and the complicated etching technique necessary to reveal clearly the presence of microconstituents in the various zones of the Pt-Al coating. A typical SEM photomicrograph of an inward Pt-Al coating is shown in Figure 2 which exhibits the four zone structure. The surface zone is Pt-rich single $PtAl_2$ phase. As mentioned earlier, the outer intermediate zone consists of fine platinum-rich $PtAl_2$ and refractory metal enriched precipitates in an NiAl matrix rich in Al. It should be noted that the fine $PtAl_2$ precipitates are present in the upper region while refractory metal enriched precipitates are present in the lower portion. However, the volume fraction of these (refractory metal enriched) precipitates in an NiAl matrix is increased substantially as Ni content increases in the NiAl phase. The inner intermediate zone is a single phase NiAl containing high nickel and the innermost zone is the interdiffusion zone.

As pointed out earlier, outward type Pt-Al coating structures are produced by a HTLA process. Like the inward type structure, the diffusional interactions among the elements during the low activity

aluminizing process are also very complicated. Aluminum apparently diffuses inward until it forms a single NiAl phase containing low Pt and Al through which essentially only Ni (not Al) diffuses outward from the substrate to the pre-diffused Pt enriched layer, thus resulting in a lower Al gradient across the Ni-Al coating. Furthermore, platinum diffusion continues during the aluminizing process, and it is limited near the substrate at much higher temperature for longer times presumably by the outward flux of Ni. The actual Al and possible Ni level were found to be extremely important in influencing the relative movement of the elements and the resulting phase distribution. However, the observation of diffusion of platinum through the NiAl (containing low Al) is still considered significant and is an area of active investigation. Present understanding and speculation in this area will be presented later.

Figure 3 illustrates typical optical photomicrographs of the outward type Pt-Al structures given various pre-aluminizing diffusion heat treatments. Figure 3(a) exhibits a typical two-zone structure. The surface zone consists of platinum rich $PtAl_2$ phase and the inner zone is the interdiffusion zone. Figures 3(b) and 3(c) exhibit typical three-zone structures. The surface zone consists of Pt-rich precipitate (i.e., $PtAl_2$) in the Al rich NiAl matrix while the intermediate zone is a single phase NiAl rich in nickel, denuded of any other phases or substrate elements. It should also be noted that the $PtAl_2$ in this structure is not a continuous phase although in some structures it appears to be and this difference in distribution is an area for further evaluation and clarification. The formation mechanisms of fine $PtAl_2$ precipitates in Al rich NiAl matrix is not yet understood but may be related to the pre-aluminized diffusion structure. It is reported (20) that the

structure of Pt-Al coatings produced by HTLA process changes from a single phase to two phase structure with increasing pre-aluminizing diffusion time and temperature, as determined by x-ray diffraction analysis. The x-ray data are also listed in Table II.

Therefore, the microstructure of Pt-Al coatings produced either by the LTHA or HTLA process is strongly dependent on such factors as, (1) the amount of platinum (although not an intentional variable in this study), (2) the pre-aluminizing diffusion time and temperature and the resulting structure, (3) the aluminum activity level and the time and temperature condition of the aluminizing process. As an example, Figures 4(a) and 4(b) exhibit structural changes as a result of variations of the pre-aluminizing time, temperature and aluminum activity level. Figure 4(a) exhibits the typical single phase $PtAl_2$ in the outer zone of an inward Pt-Al coating while Figure 4(b) depicts a typical two phase ($PtAl_2$ plus NiAl matrix) structure in the outer zone of an outward type Pt-Al coating.

Streiff, et al. (20) have also reported that the oxidation behavior of Pt modified aluminide coatings is significantly dependent on the structure, i.e., the amount and the distribution of Pt (and possible Al level) in the coating. The effect of prolonged annealing in air at 1080° C of two commercial Pt-Al coatings is shown in Figures 5 and 6. It can be noted that the single phase inward Pt-Al coating (Figure 5(a)) did not change structure during prolonged annealing (i.e., 24 hours) at 1080° C (Figure 5(b)) while the initial two phase structure shown in Figure 6(a) in the outer zone of the outward type Pt-Al coating rapidly changes to the single phase structure shown in Figure 6(b) during prolonged exposure (24 hours) at 1080° C. Although, in coatings produced by the high activity

process, the structure did not change during the 24 hours treatment, the composition across the coating will not remain the same and a structural transition will occur, apparently at some critical Al level. Prolonged annealing produces a more uniform single phase structure and elemental distribution in the outer zone of low activity Pt-Al coatings. The Al level of the NiAl is now postulated to affect the movement of Pt as it does for Ni and Al and hence initial coating Al contents can have a significant effect on the system's structural and diffusional stability.

Summarizing the x-ray diffraction and electron probe data of two structural types of Pt-Al coatings, it is found that the diffusional interaction between the elements present in the coatings and in the substrate is very complex in nature. In the following paragraphs, the formation mechanisms of these coatings as they are presently understood will be discussed in greater detail. As presented earlier, pre-aluminizing treatments produce a higher concentration of Pt near the surface. The extent of Pt diffusion is strongly dependent on the amount of time and the pre-aluminizing temperature. Figure 7(a) presents an initial schematic representation of Pt diffusion during heat treatment. A typical elemental distribution across an inward type Pt-Al coating is shown in Figure 7(b). It is further important to note that as a result the Pt concentration profile is relatively flat to about 25 μm of the final coating thickness followed by a sharp drop in concentration level to zero. At these lower pre-aluminizing temperatures, platinum interdiffusion is not significant. Therefore, a high level of Pt is available near the surface to interact with the incoming aluminum atoms during the aluminizing treatment and thus produces a continuous $PtAl_2$ phase during the LTHA aluminizing process. With longer diffusion times at

higher temperatures prior to aluminizing the Pt is distributed over a wider zone near the surface and the surface Pt content is lower.

Figure 7(c) illustrates the elemental distribution across the outward type Pt-Al coating. It is important to note here that the Pt concentration decreases gradually from the surface to a minimum near the substrate followed by a small peak in the interdiffusion zone near the interface between the substrate and the coating while the Ni concentration profile maintains a fairly high level close to the surface (see Figure 7(c)). The Al concentration profile is also found to decrease (not as fast as Pt) from the surface to near the interface. The initial level of Al available in the HTLA process (see Figure 7(c)) is also less than that in the LTHA process (see Figure 7(b)), as expected from the aluminum activity level in the pack. However, the presence of a sufficiently high level of Pt near the surface can interact with the (presumed) incoming Al atoms and thus results in $PtAl_2$ phase (either as formed or precipitated during subsequent cooling). These fine discontinuous $PtAl_2$ phase precipitates are present in Al-rich NiAl phase. The formation of Al rich NiAl phase (as opposed to the continuous $PtAl_2$ layer) is mainly the result of the high level of Ni (i.e., about 40%) near the surface which thus interacts with the available Al atoms.

The simultaneous diffusion of Pt and Ni through the NiAl phase during the HTLA process is also very complex. Figure 8 is a schematic representation of possible platinum diffusion effects for the NiAl phase component. Elegant measurements of D_{Al}/D_{Ni} have been made in the Al-Ni system (25). It is reported that the Ni is the predominant diffusing constituent in hypo-stoichiometric NiAl while in hyper-stoichiometric NiAl, Al becomes the predominant diffusing species. Therefore, it is of

interest to speculate as to the the effect of Pt additions to the Al-Ni system at 1150° C. The solid lines in Figure 8 show the interdiffusion coefficient ratio of D_{Al}/D_{Ni} in an Al-rich NiAl which contains a large number of lattice vacancies. Pt additions to Al-Ni system are found experimentally in these studies to move these interdiffusion coefficient ratio lines toward the left (i.e., towards lower Al levels) as shown with the broken line. The extent of this shift has not yet been established but it is now postulated to be a strong function of Pt level. Pt addition to NiAl reduces the apparent Al content of NiAl at which Al is the dominating diffusional element. Then apparently once the β (NiAl) composition falls below a critical Al level (i.e., a new stoichiometry of the ternary NiAl containing Pt), Pt can diffuse very rapidly (as does Ni in pure NiAl) and the $PtAl_2$ phase is not stable.

B. HOT CORROSION DATA

1. High Temperature

Recently Deb, et al. (26) reported that the low aluminum activity process, in general, appears to be less sensitive to surface attack at 900° C as compared to samples produced by the high aluminum activity process (Note: in this study the HTLA coating was applied in the vapor phase, so-called out-of-the pack and the effect of this variable has yet to be assessed). However, surface degradation of both types of platinum aluminide coatings is very severe as is observed in Figure 9 when both the specimens were given a prolonged pre-aluminizing diffusion heat treatment (i.e., 1080° C for 4 hrs.). Even with this diffusion treatment, however, specimens given either LTHA or HTLA aluminizing treatments were attacked at a rate of only 0.2 μm/hour, at least a factor of six times

more corrosion resistance than the unmodified aluminides (1.5 μm/hour) exposed in the same test as control samples.

The increased surface degradation behavior of both the HTLA and LTHA type coatings after prolonged diffusion may probably be the results of the formation of the two-phase structure in the outer zone. It is reported that the single phase structure is produced in the outer zone of both the coatings when the specimens are given 0.5 hours pre-aluminizing diffusion at 870° C.

2. Low Temperature

Streiff, et al. (21) and Deb, et al. (26,27) have studied the hot corrosion behavior of platinum modified aluminide coatings on the IN-738 superalloy substrate at 700 and 900° C respectively. In these studies (24,30,31) it is observed that the addition of platinum to a standard aluminide is not found to be beneficial at 700° C (i.e., about a two-fold impact) as compared to hot corrosion behavior of platinum additions at 900° C (i.e., a six-fold increase). However, they have reported that the three-zone inward type coating showed much less attack than the standard two-zone outward type coatings. They have also noted that a continuous, pure, $PtAl_2$ phase, shown in Figure 10(a), is present in the more resistant coatings. In low temperature hot corrosion environments, this continuous $PtAl_2$ layer apparently prevents (i.e., acts as a barrier to) hot corrosion attack. Figure 10(b) exhibits a typical low temperature hot corrosion attack.

Recently Dust, et al. (28) have studied the low temperature hot corrosion behavior of platinum-aluminide and chromium modified platinum-aluminide coatings at 700° C in an air:SO_2 (i.e., 2000ml/min.: 5 ml/min.) environment on the IN-100 superalloy substrate. They have

reported that the LTHA platinum-aluminide coating did not display particularly good resistance to LTHC (i.e., about 50 μm minimum penetration in 100 hours) as compared to HTLA platinum-aluminide coatings. However, the LTHA platinum-aluminide coating showed (i.e., 0.5 μm/hour surface attack) little improved LTHC resistance (i.e., two-fold) over the unmodified-aluminide coatings (1.0 μm/hour) at 700° C reported by Deb and Boone (27). This is also consistent with the above results (21,26) reported here. Although this sample had a surface layer of $PtAl_2$ as shown in Figure 11(a), there was little improved LTHC resistance (see Figure 11(b)) over the HTLA platinum-aluminides. The two HTLA platinum-aluminide coatings did provide a good resistance to LTHC attack (i.e., about 40 μm minimum penetration) and it is interesting to note that a thick two-phase structure of $PtAl_2$ and β-NiAl (Al-rich) was present underneath the thin surface layer of $PtAl_2$. Even after this surface layer was penetrated, the Pt-rich $PtAl_2$ precipitates provided some hot corrosion resistance. In other testing (11,27,30,31) the continuous $PtAl_2$ layer has been reported as the LTHC resistant structure with the two-phase $PtAl_2$/ β-NiAl structure performing little better than the unmodified-aluminide. Recently Dust, et al. (28) and Deb, et al. (29) noted that the Pt diffusion through the hypo-stoichiometric NiAl composite is not yet well understood but it is apparently a strong function of Al level. It appears that once the β-NiAl composition falls below a critical Al level (i.e., a new stoichiometry of the ternary NiAl containing Pt), Pt can diffuse very rapidly (as does Ni in hypo-stoichiometric β-NiAl) and thus $PtAl_2$ becomes unstable. This could be one of the reasons why the LTHA platinum-aluminide coating, even though it had a thick (i.e., about 20 μm) continuous layer of $PtAl_2$ at

the surface, did not show good resistance to LTHC attack as compared to the HTLA platinum-aluminide coatings. In these tests, the coating's lifetime may be dependent on the optimum thickness and stability of this $PtAl_2$ surface layer.

The chromium-modified platinum-aluminides also differed greatly in LTHC resistance. Process D (Cr-Pt-Al) which exhibited a good LTHC resistance (about 34 μm penetration), had a high $PtAl_2$ surface content with little Ni or Cr, again confirming the observation that a continuous single $PtAl_2$ phase at the surface is beneficial. Process B (Pt-Cr-Al), which exhibited poor resistance to LTHC attack (about 66 μm penetration), had less continuous $PtAl_2$ phase with high amounts of Ni (probably NiAl) and some chromium. In both coatings, the most important factor for the LTHC resistance appeared to be the $PtAl_2$ content at the surface layer because they both had a relatively high level of chromium concentration near the surface. Applying chromium first and then platinum prior to aluminizing allows an effective layer of $PtAl_2$ to form at the surface, while reversing the alloying addition sequence (i.e., Pt-Cr-Al) disperses the Pt in the intermediate zone. As a result, a continuous single $PtAl_2$ phase cannot form at the surface during subsequent aluminizing and post-aluminizing heat treatment. It is therefore important to emphasize that the structure of these chromium-modified platinum-aluminides is strongly dependent on the modifying element which is first applied.

C. CYCLIC OXIDATION

It is known that pre-aluminizing diffusion heat treatments produce an exaggerated micro-surface roughness on the platinum modified aluminide coatings, as compared to the un-modified coatings. Recently, the effects

of surface structure under cyclic oxidation at 1100° C of the two structural groups of unmodified and platinum modified aluminide coatings were studied (24). In that investigation, variously heat treated platinum free and platinum modified aluminide coatings were exposed to cyclic oxidation environment at 1100° C for times up to 250 hours. The specimens were cycled for 60 minutes at 1100° C and then cooled 10 minutes outside the furnace prior to reheating. It was found that surface plastic instability occurred, called "rumpling", shown in Figure 12(a) and 12(b), and that the degree of rumpling was observed more in the platinum modified aluminide specimens. Figure 12(c) shows SEM photomicrograph of the corresponding cross-section. Surface upheavals on the order of 50 μm were found on both systems. The amount of surface rumpling during cyclic oxidation testing can be attributed to several factors such as coefficient of thermal expansion mismatch between coating and substrate, thermal gradients across the specimen (i.e., thermal strains) produced during heat and cooling, coating strength which depends on the microconstituents and composition present in the coating, and finally, the coating thickness (which also affects coating composition and structure). Therefore, the resulting performance of the coatings is a complex interplay of the above mentioned variables. At present, there is no mention in the literature of surface rumpling of the platinum aluminide coatings or even of the unmodified aluminides. However, similar surface rumpling has been reported on some overlay MCrAlY coating system.

In this study, it was established that the rumpling observed could not be attributed to simple coating affected substrate melting. It was, however, observed that the platinum modified aluminide coatings did not show oxide spallation and that oxide spallation of the un-modified

coatings appeared with a secession of further rumpling. Finally it was found that the thicker coatings on the IN-738 substrate showed a lower propensity to rumple as compared to the thinner coatings. However, for the thick coating samples which showed minimum rumpling, transverse coating cracks were found while no such cracks were observed in the thinner coatings which underwent significantly more plastic deformation. Further studies of this phenomena and the variables operating are underway.

D. MECHANICAL PROPERTIES

As mentioned earlier, a wide range of structures and compositions of Pt-Al coatings can be prepared by varying the pre-aluminizing and post-aluminizing diffusion heat treatments. There are several variables which directly or indirectly control the coating performance under severe environmental conditions. It is therefore expected that the mechanical properties of diffusion type coatings such as the Pt modified aluminides will depend on the type of structure and the corresponding elemental distribution within the coating as well. There are however, little data available on the mechanical properties of the platinum modified aluminides and none relating to specific structures. There are only limited data available on the un-modified aluminides (32-34) and the overlay type MCrAlY coatings (35).

It is reported (24) that in high temperature cyclic testing, the platinum modified aluminides showed surface rumpling which is mainly attributed to the coefficient of thermal expansion mismatch induces strains between the coating and the substrate. It is also known that the coating's ability to accommodate additional strain is its ductility.

Therefore the ductile to brittle transition temperature (DBTT) of these coatings is very important so far as coatings mechanical properties and the engineering design of coated components is concerned.

Recently Vogel (36) has studied the DBTT of several structural variations of the Pt-Al coatings. It was found that the DBTT is strongly structural dependent. It is also interesting to note that the DBTT of outward type Pt-modified aluminides (i.e., HTLA) is in the range of 640-700° C, while inward diffusion type Pt-modified aluminides did not show DBTT up to the maximum experimental temperature (i.e., 800° C) shown in Figure 13. As might be expected, the data reveal that structures with high Pt concentrations near the surface and high Al levels have higher DBTT's. Lower Al levels and two-phase structures (i.e., $PtAl_2$ plus NiAl) which are generally provided by the HTLA coating process are more ductile. Because it is difficult to separate out the platinum, aluminum and structural effects which are produced by the various aluminizing treatments, additional testing and more detailed structural characterization is underway.

A high DBTT of any given coating is undesirable since the coating remains in the brittle mode for a longer period of time as compared to a coating which has a lower DBTT. A low DBTT will place the coating substrate system into a ductile mode at lower operating temperatures. Therefore the probability of cracking type failure for a low DBTT coating is much less than in high DBTT coating when turbine engine experienced various spectrum loading over a wide range of temperatures under hostile environments. Optical metallographic examination of these tested Pt-Al specimens revealed wide and well spaced cracks in the coatings tested above the DBTT while the inward and the outward type coatings tested below

the DBTT exhibited straight, very fine and closely spaced cracks. These observations are also in good agreement with the published crack morphology data of the unmodified aluminides (36-38). Even though the high Al and Pt content coatings exhibited a high DBTT, their room temperature ductility appeared greater than that of the "more ductile" coatings. Initial analysis has related this to a high level of residual compressive stress in the coatings at room temperature, the higher Al and Pt content coatings having the higher compressive stresses. The magnitude of these stresses and their effects on handling and rumpling properties are being investigated, but a strong correlation is postulated.

E. CONCLUSIONS

The following salient conclusions are the outcome of FY85 research effort*:

1. Hot Corrosion

The presence of platinum in an aluminide coating improves hot corrosion resistance at 900° C; the degree of improvement depends on the structures and possible processing parameters. Low aluminizing activity processes (i.e., HTLA) apparently produces coatings with improved hot corrosion resistance over those produced by the high aluminum activity process (i.e., LTHA). In low temperature hot corrosion little benefit (about 2.5 times improvement) of platinum additions were found over the unmodified aluminide coatings.

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*FY81-FY84 research results are already published (see Appendix II - publication #1 to 7.

2. Cyclic Oxidation

In an initial cyclic oxidation test, it is found that cycling to elevated temperature produces surface rumpling in both unmodified and platinum modified coatings. The degree of rumpling is a function of platinum level and structure and appears related to coefficient of thermal expansion mismatch induced strains and coating properties.

3. Mechanical Properties

At comparable aluminum levels, the presence of platinum increases the DBTT and room temperature residual compressive stress level. DBTT and residual stress can be varied by changing the composition and structure of the coating.

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APPENDIX I

The following scientists and students were directly involved in this program:

Lawrence Berkeley Laboratories, University of California, Berkeley, California

Prof. R. Streiff, Prof. D. P. Whittle, R. T. Lambertson, D. A. Crane, and Ms. L. J. Purvis.

Mechanical Engineering Department, Materials Science Group, Naval Postgraduate School, Monterey, California

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APPENDIX II

The following publications and presentations are the output of the research funding sponsored by the Office of Naval Research under Contract No. N0001485WR24098 during 1981 to 1985.

PUBLICATIONS

1. The Effect of Deposition and Processing Variables on the Oxide Structure of MCrAl Coatings, Boone, D. H., Lambertson, R. T., Shaffer, S. and Peacock, D. E., presented at the International Conference on Metallurgical Coatings, 18-22 April 1983 and published in Thin Solid Films, 107, pp. 463-472, 1983.

2. Structures of Platinum Modified Aluminide Coatings, Boone, D. H., Streiff, R. and Purvis, L., presented at NATO Advanced Study Institute on Surface Engineering, Les Arcs, July 1983 and published in the proceedings.

3. Les Revetements d'Aluminiures Modified par le Platine: un Nouveau type de Revetements Proctecteurs Contre la Corrosion, Boone, D. H., Streiff, R. and Purvis, L., presented at the Societe Francaise de Metallurgie, Paris, France, 18-20 December 1983 and published in the Journees Metallurgiques d'Automne.

4. Erosion of Conventional and Ultrafine Grain Materials, Boone, D. H., Hicky, G., Levy, A. and Stiglich, J. J., presented at the International Conference of Metallurgical Coatings, San Diego, CA, 9-13 April 1984 and published in Thin Solid Films, 118, No. 3, pp. 321-333, 1984.

5. A Long Term Field Test of Advanced Gas Turbine Airfoil Coatings Under a Severe Industrial Environment, Boone, D. H., Kubarych, K. G. and Duncan, R. L., presented at the 1984 ASME Gas Turbine Conference, Amsterdam, the Netherlands, 3-7 June 1984 and published as ASME 84-GT-277.

6. The Surface Morphology of Diffusion Aluminide Coatings, Boone, D. H., Streiff, R. and N'Gandu Muamba, J. M., presented at the International Conference on Metallurgical Coatings, San Diego, CA, 1984 and published in Thin Solid Films, 119, 1984, pp. 291-300.

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APPENDIX II

8. Platinum Aluminide Structural Effects on Hot Corrosion Resistance at 900° C, Deb, P., Boone, D. H., and Streiff, R., presented at the 12th International Conference on Metallurgical Coatings, Los Angeles, CA, April 1985 and published in JVSTA, Nov-Dec 1985.

9. Surface Morphology of Platinum Modified Aluminide Coatings, Boone, D. H., Deb, P., Purvis, L. J. and Rigney, D. V., presented at the 12th International Conference on Metallurgical Coatings, Los Angeles, CA, April 1985 and published in JVSTA, Nov-Dec 1985.

10. Effect of Microstructural Morphology on the Performance of Platinum Aluminide Coatings, Deb, P., Boone, D. H., and Streiff, R., presented at the International Conference on Metallurgical Coating, Toronto, Canada, October, 1985 and will be published in ASM Technical Paper.

11. Hot Corrosion Resistance of Chromium Modified Platinum Aluminide Coating, Dust, M., Deb, P., Boone, D. H., and Shankar, S., to be presented at the June 1986 Gas Turbine Conference, Dusseldorf, W. Germany and will be published in ASME Technical Paper.

12. Structure and 700° C Hot Corrosion Behavior of Chromium and Platinum Modified Aluminide Coatings, Deb, P., Boone, D. H., Dust, M., and Shankar, S., to be presented at the 13th ICMC, San Diego, California, March 1986 and will be published in the proceedings.

13. Surface Instability of Platinum Modified Aluminide Coatings During 1100° C Cyclic Testing, Manley II, T. F., Deb, P., and Boone, D. H., to be presented at the 13th ICMC, San Diego, California, March 1986 and will be published in the proceedings.

14. Platinum Aluminide Structural Effects on Hot Corrosion Resistance at 700° C, Deb, P. and Boone, D. H., to be published, 1986.

PRESENTATIONS

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9. The Effect of Aluminide Processing Variables on Oxide Structures, Boone, D. H. and Lambertson, R. L., presented at the Fall AIME Meeting, St. Louis, MO, 25 October 1982.

10. Structural Variations in Platinum Modified Aluminide Coatings, Boone, D. H. and Purvis, L. J., presented at the Fall AIME Meeting, St. Louis, MO, 25 October 1982.

11. Protective Oxide Characterization of Mn Modified Aluminide Coatings, Boone, D. H., Lambertson, R. L. and Barber, M. J., presented at the Fall AIME Meeting, St. Louis, MO, 25 October 1982.

12. Repair Coatings, Boone, D. H., presented at the Electrochemical Society Boston Meeting, the Fundamental Aspects of Coatings Session, Boston, MA, October 1982.

13. Turbine Protection Systems and Implications of Other Propulsion Applications, Boone, D. H., seminar, Materials Science Laboratory, Aerospace Corporation, El Segundo, CA, 9 February 1983.

14. Erosion of Hard Metal and Ceramic Coatings, Boone, D. H., Levy, A. and Kelley, J., presented at the TMS-AIME Annual Meeting, Atlanta, GA, 6-10 March 1983.

APPENDIX II

15. Effect of Coating Processing Techniques on Superalloy Properties, Boone, D. H., presented at the ASME 28th International Gas Turbine Conference, Phoenix, AZ, 30 March 1983.

16. Erosion Behavior of Ceramic Coatings, Boone, D. H. and Lambertson, R. T., presented at the International Conference on Metallurgical Coatings, San Diego, CA, 18-22 April 1983.

17. The Effect of Aluminide Processing Variables on the Oxide Structure Using the Deep Etch Technique, Boone, D. H. and Lambertson, R. T., presented at the International Conference on Metallurgical Coatings, San Diego, CA, 18-22 April 1983.

18. Hot Corrosion Resistance of Modified Aluminide Coatings, Boone, D. H., Peacock, D. E. and Rose, B. R., presented at the International Conference on Metallurgical Coatings, San Diego, CA, 18-22 April 1983.

19. The Formation and Structure of Platinum Modified Aluminide Coatings, Boone, D. H., Purvis, L. and Streiff, R., presented at the International Conference on Metallurgical Coatings, San Diego, CA, 18-22 April 1983.

20. Structure and Erosion Behavior of an Ultrafine Grained SiC, Boone, D. H. and Stiglich, Jr., J. J., presented at the American Ceramic Society Meeting, Chicago, IL, 26 April 1983.

21. The Protective Oxide Structures of Thermal Spray Applied MCrAl Coatings, presented as poster at the 10th International Thermal Spraying Conference, Essen, West Germany, 2-6 May 1983.

22. Wear of Protective Coating Systems, Boone, D. H., Levy, A. V. and Davis, A., presented at TMS-AIME General Abstract Session, Fall Meeting, Philadelphia, PA, October 1983.

23. The Role of Hf as Active Element in Oxidation Resistant Coatings, Boone, D. H. and Streiff, R., presented at the High Temperature Erosion and Corrosion Symposium of the High Temperature Materials and Corrosion Division, Electro-Chemical Society, Washington, DC, 9-14 October 1983,

24. The Development of Chromium Coatings, Boone, D. H., Streiff, R. and Godlewska, E., presented at the High Temperture Erosion and Corrosion Symposium of the High Temperature Materials and Corrosion Division, Electro-Chemical Society, Washington, DC, 9-14 October 1983.

APPENDIX II

25. Plasma Spray Coating Experience in Diesel Engines, Kvernes, I. and Boone, D. H., presented at the 7th Annual Energy-Source Technology Conference and Exhibition, New Orleans, LA, 12-16 February 1984.

26. Results of Combustion Zone Durability Program, Levy, A. and Boone, D. H., presented at the 7th Annual Energy-Source Technology Conference and Exhibition, New Orlenas, LA, 12-16 February 1984.

27. Surface Structural Effects on Pt Modified Aluminides, Boone, D. H., Purvis, L. and Rigney, D. V., presented at the International Symposium on Precious Metals, 113th AIME Annual Meeting, Los Angeles, CA, 26 February-2 March 1984.

28. Plasma Spray Surface Processing Effects on Oxide Adherence, Boone, D. H., Norton, P. R., Peacock, D. E. and Rigney, D. V., presented at the 113th AIME Annual Meeting, Los Angeles, CA, 26 February-2 March 1984.

29. 700° C Hot Corrosion Resistance of Pt Modified Aluminides, Boone, D. H., Purvis, L. and Peacock, E. E., presented at the 113th AIME Annual Meeting, Los Angeles, CA, 26 February-2 March 1984.

30. The Protective Coating of ODS/MA Superalloys, Boone, D. H., Brown, Boveri and Cie Seminar, Baden, Switzerland, 26 March 1984.

31. Advances in Superalloy Coating Science and Technology, Boone, D. H., Fiat Research Laboratory Seminar, Turin, Italy, 28 March 1984.

32. Structure Protection Relationships for Platinum Modified Aluminide Coatings, Boone, D. H., Streiff, R. and Peacock, D. E., presented at the Coatings for Heat Engines, NATO Advanced Workshop, Italy, 1-6 April 1984.

33. Interaction of Coating Systems with Substrate in Engine Applications, Boone, D. H., presented at the Coatings for Heat Engines, NATO Advanced Workshop, Italy, 1-6 April 1984.

34. High Temperature Corrosion Resistant Platinum Modified Coatings for Superalloys, Boone, D. H. and Streiff, R., presented at the 9th International Congress on Metallic Corrosion, Toronto, Canada, 4-7 June 1984.

35. Protectivity of Platinum Modified Aluminide Coatings, Boone, D. H., presented at panel on "Coatings, Corrosion and Repair", ASME Gas Turbine Conference, Amsterdam, the Netherlands, June 1984.

APPENDIX II

36. EB Coatings on Repaired Blades, Boone, D. H. and Halnan, W. K., presented at the REP-TECH '84 Jet Engine repair Technology Workshop, San Antonio, TX, 15-17 October 1984.

37. The Evolution and Revolution in Coatings for Gas Turbines, Boone, D. H., invited speaker, ASM meeting, San Antonio, TX, 18 October 1984.

38. High Temperature Coating Processing for Jet Engine Repair Workshop, Boone, D. H. and Rigney, D. V., course directors and lecturers, San Antonio, TX, 18-19 October 1984.

39. Research Activities in High Temperature Protective Coating Systems, Boone, D. H., seminar of University of Minnesota, Department of Materials Science, 3 May 1985.

40. Advanced Coatings for High Temperature Corrosion Protection of Gas Turbine Materials, Boone, D. H., Seminaire De Chimie Des Materianx, Universite De Provence, Marseille, France, 28 Mai 1985.

APPENDIX III

The following ongoing research are in progress:

ABROAD

1. Australia, Dr. Johnston - Rutherford Backscattered (RBS) analysis of platinum modified aluminides; initial stages of oxide formation.

2. University of Nancy, France, Dr. Steinmetz - Fused salt corrosion testing.

3. Universite de Provence, France, Prof. Streiff - Phase diagram consideration.

4. Institute of Metals Achedemia Since, China, Prof. Wu - Surface analysis of fused salt electrolysis and initial stages of oxide formation.

NAVAL POSTGRADUATE SCHOOL, MONTEREY, CALIFORNIA

1. High and low temperature hot corrosion behavior of platinum and platinum chromium modified aluminide coatings on nickel and cobalt base superalloys.

2. Cyclic oxidation behavior of platinum modified aluminide coating at 1100° C as affected by surface structure.

3. Surface morphology and performance of platinum modified aluminide coatings on various superalloy substrates.

4. Determination of DBTT of platinum modified aluminide coating of various nickel base superalloy substrates.

5. High cycle fatigue response of platinum modified aluminide coatings at elevated temperature.

TABLE I. PRE-ALUMINIZING DIFFUSION HEAT TREATMENTS

HEAT TREATMENTS	TEMPERATURE, °C	DIFFUSION TIME, HOURS
I	870	0.5
II	980	2
III	1040	3
IV	1080	4

TABLE II. X-RAY ANALYSIS OF PT MODIFIED ALUMINIDE COATINGS

Aluminizing Processes:		Low Temperature High Activity, INWARD		High Temperature Low Activity, OUTWARD
Sample	Heat Treatment	As-coated	As-coated 4 hrs @ 1080° C	As-coated
IN-738		Ni_2Al_3	NiAl	NiAl
Platinum		$PtAl_2$+PtAl		$PtAl_2$
IN-738+Pt	1/2 hrs @ 870° C		$PtAl_2$	$PtAl_2$
IN-738+Pt	2 hrs @ 980° C		$PtAl_2$+ NiAl	$PtAl_2$+ NiAl
IN-738+Pt	3 hrs @ 1040° C		$PtAl_2$+ NiAl	$PtAl_2$+ NiAl
IN-738+Pt	4 hrs @ 1080° C		$PtAl_2$	$PtAl_2$+ NiAl

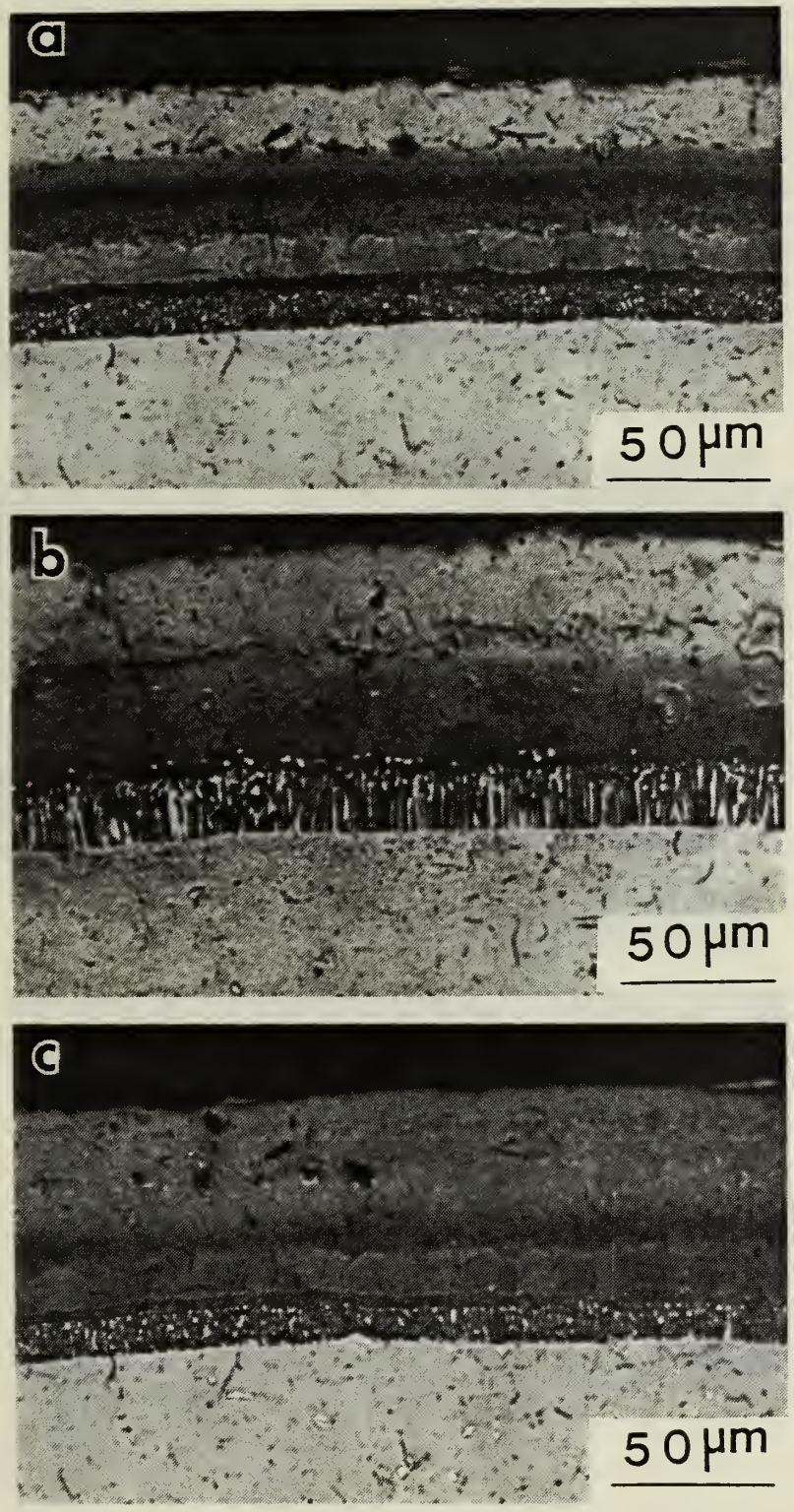

Figure 1. Typical inward type Pt-Al structures exhibit effect of pre-aluminizing heat treatments: (a) 1/2 hr. at 870° C, (b) 2 hrs. at 980° C, and (c) 1 hr. at 1050° C.

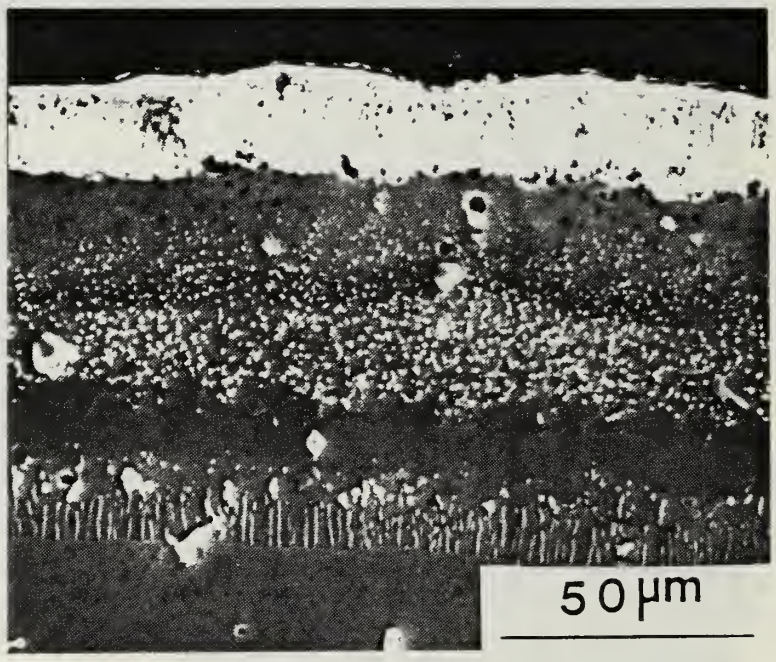

Figure 2. SEM photomicrograph of inward type Pt-Al structure contains four zones.

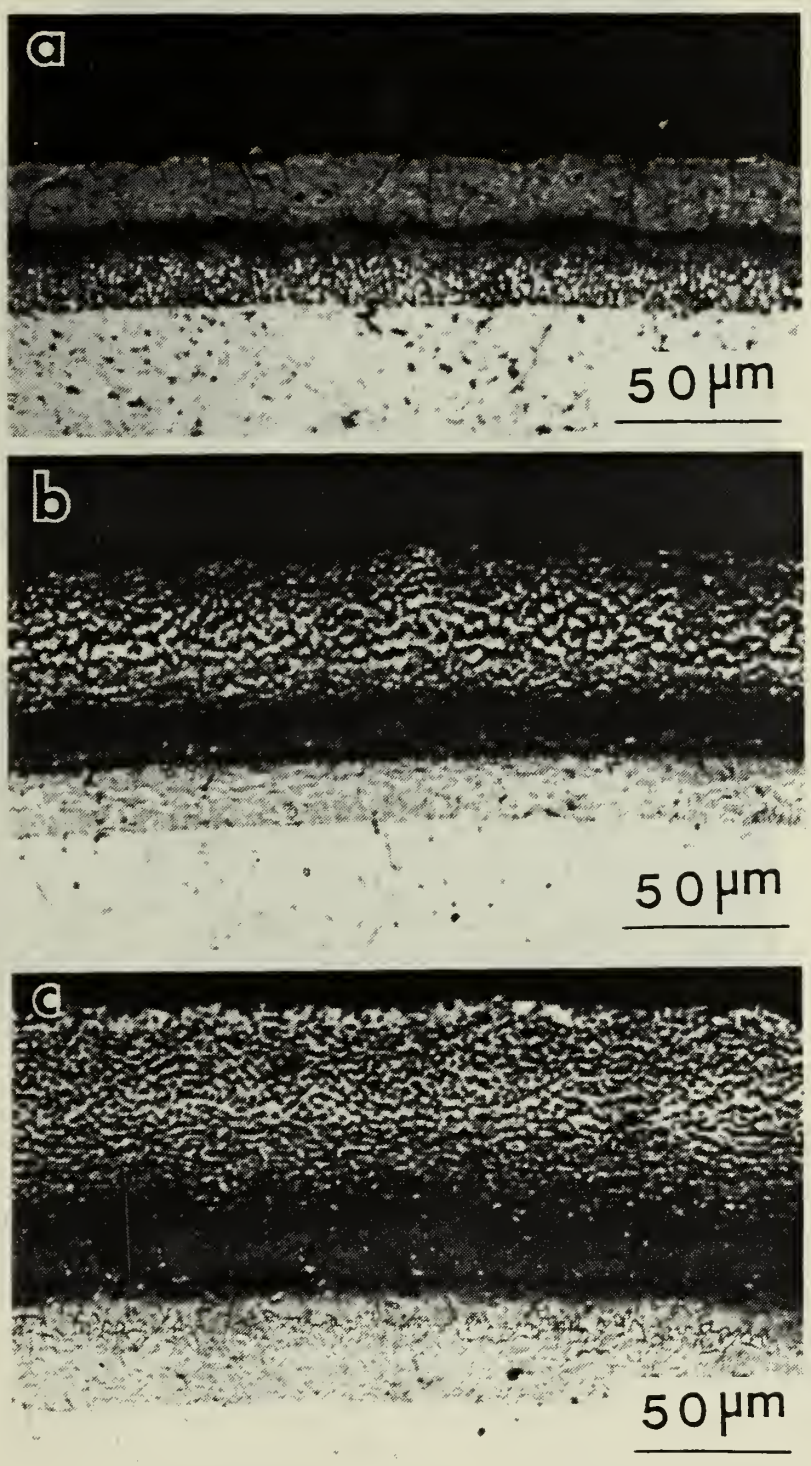

Figure 3. Typical outward type Pt-Al structures exhibit effect of pre-aluminizing heat treatments: (a) 1/2 hr. at 870° C, (b) 3 hrs. at 1040° C, and (c) 4 hrs. at 1080° C.

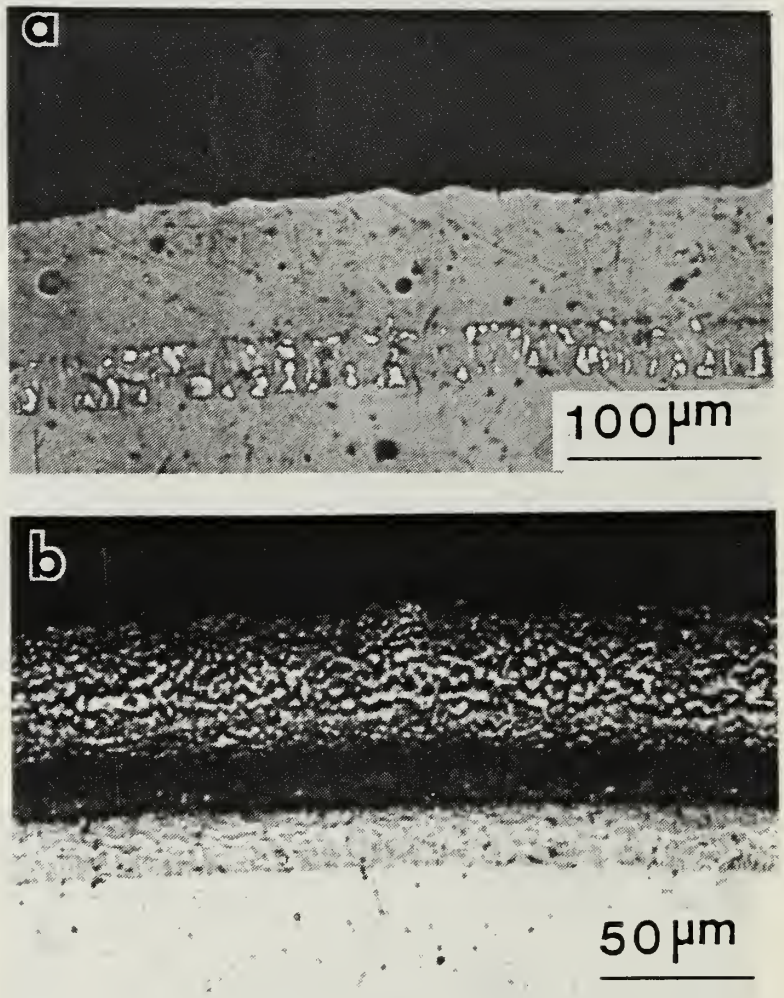

Figure 4. The outer-zone structure of Pt-Al coatings exhibit: (a) single phase, inward type structure and (b) two phase outward type structure.

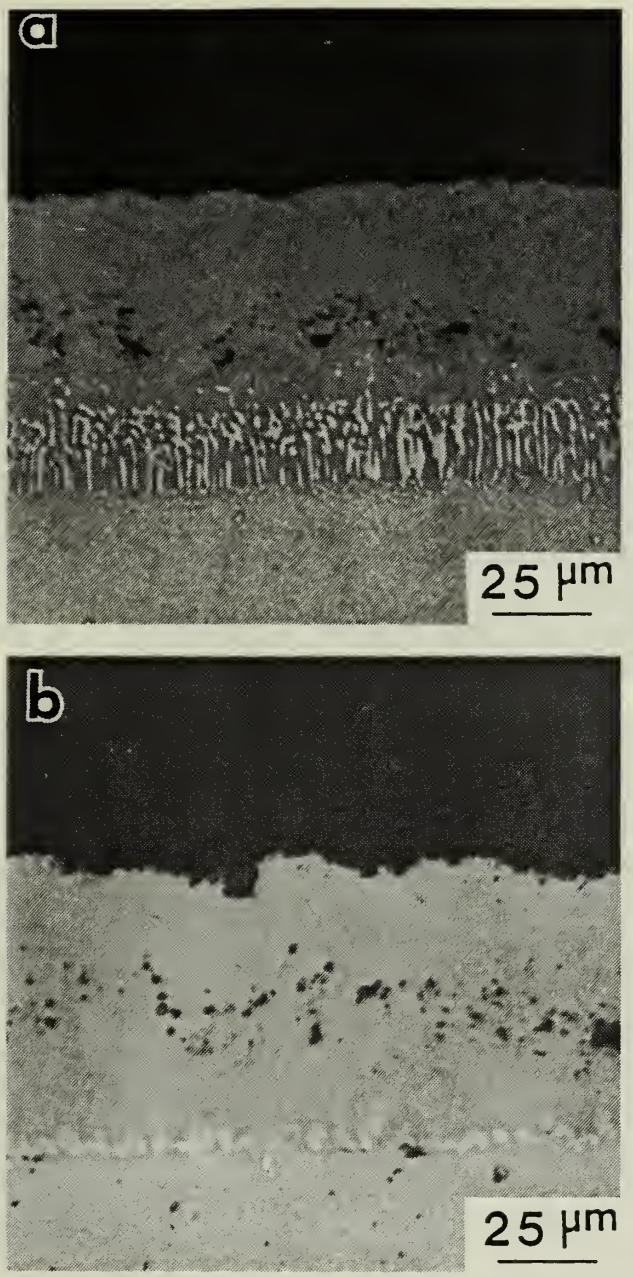

Figure 5. Effect of prolonged exposure of Pt-Al coatings in air at 1080° C exhibit: (a) single phase structure after 1 hr. heat treatment and (b) single phase structure after 24 hrs. heat treatment.

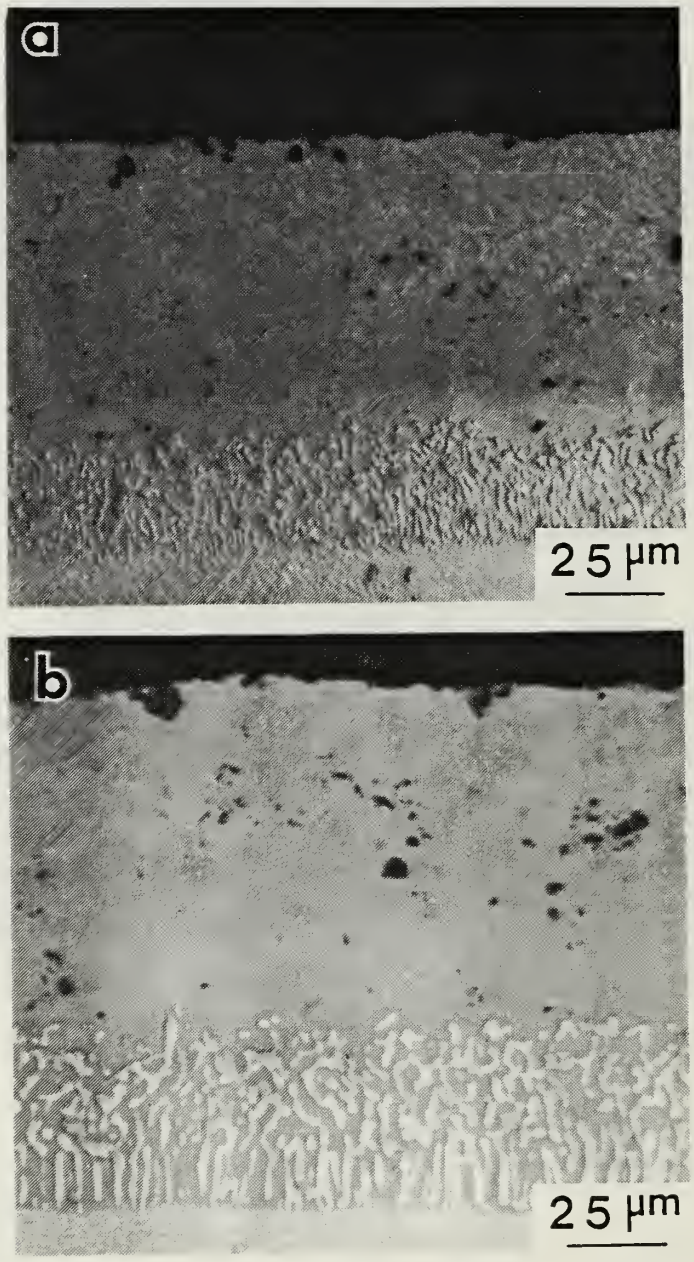

Figure 6. Effect of prolonged exposure of outward type Pt-Al coatings in air at 1080° C exhibit: (a) two phase structure after 1 hr. heat treatment and (b) single phase structure after 24 hours heat treatment.

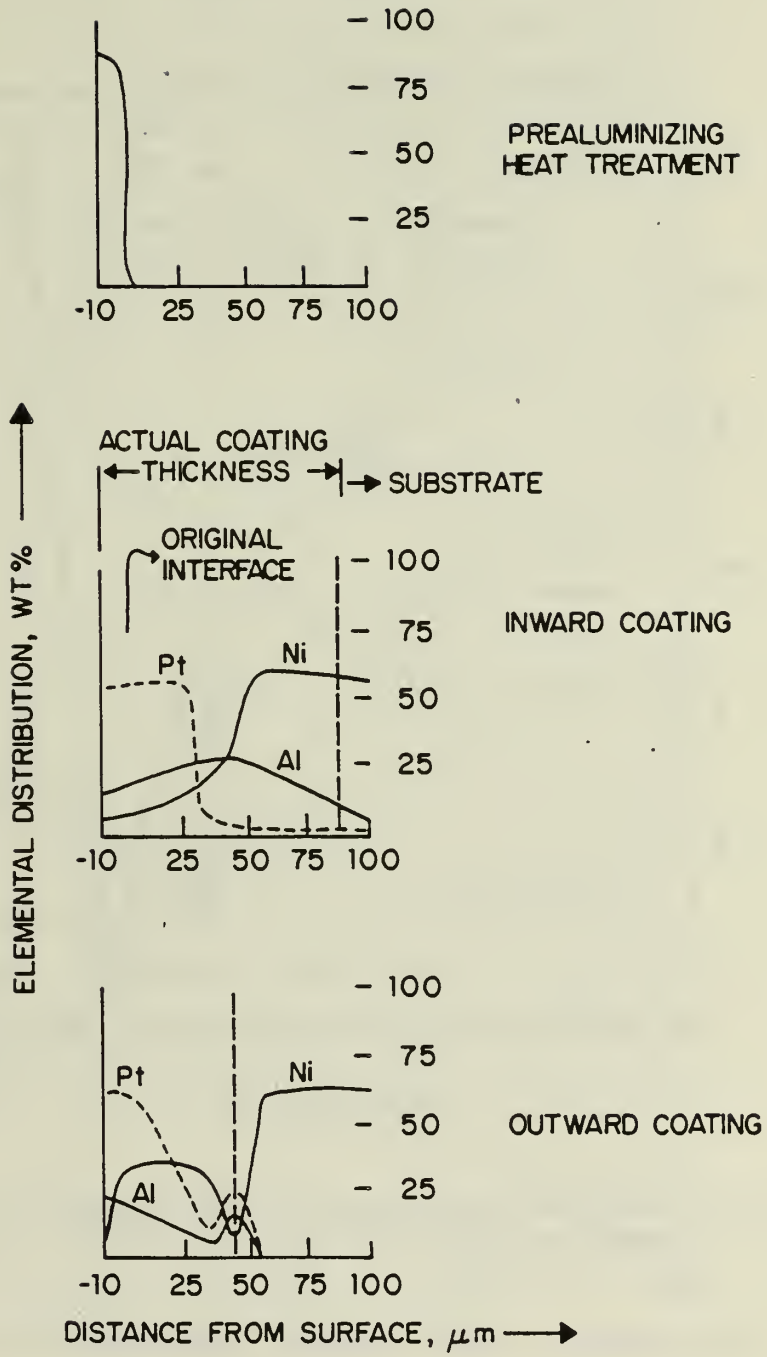

Figure 7. Elemental distribution across the Pt-Al coatings: (a) Pre-aluminizing heat treatment, 1/2 hr. at 870° C, (b) Inward type coating and (c) outward type coating.

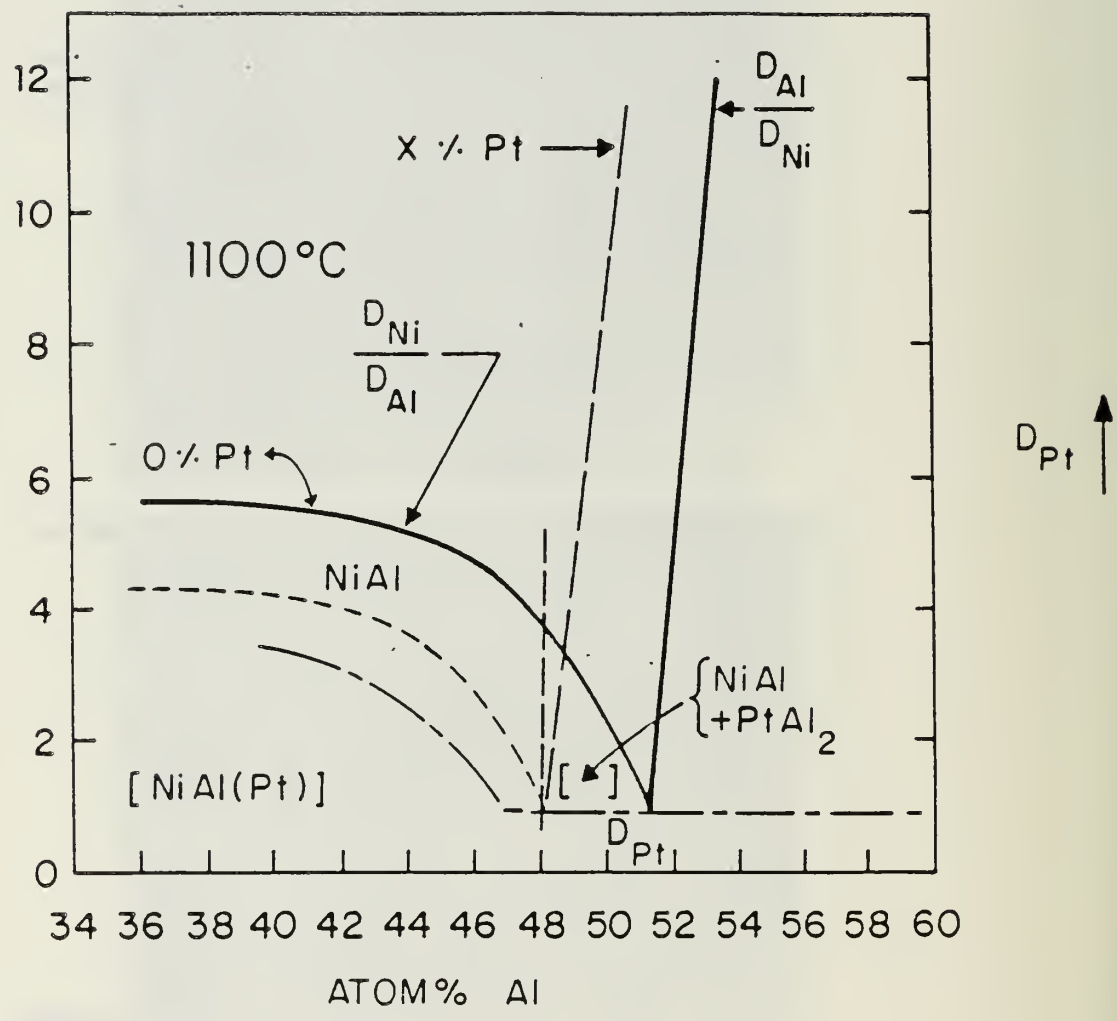

Figure 8. Possible modification of NiAl diffusion data (29) with the addition of Pt.

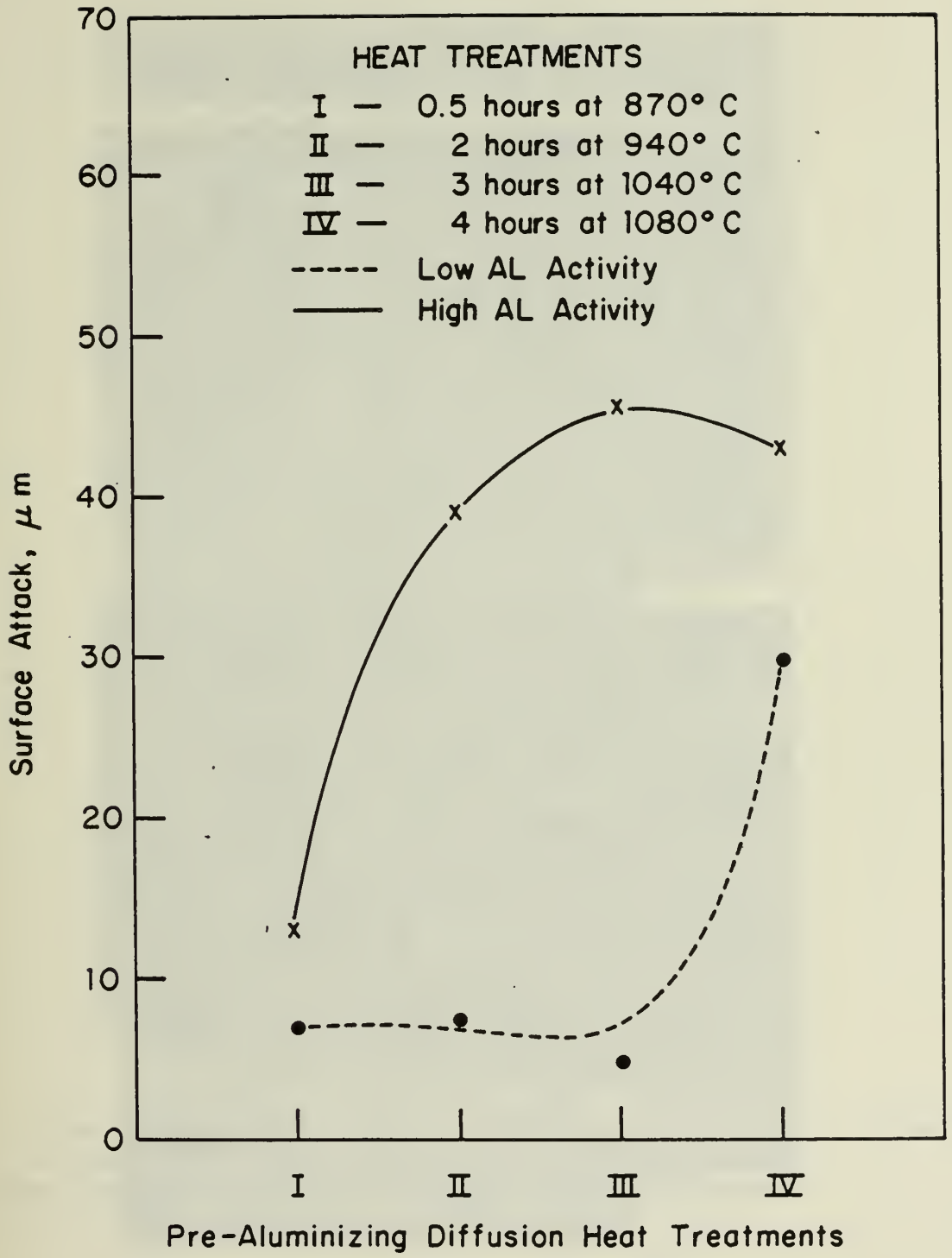

Figure 9. Surface attack of Pt modified aluminide coatings exposed for 200 hours hot corrosion condition at 900° C with various pre-aluminizing diffusion heat treatments.

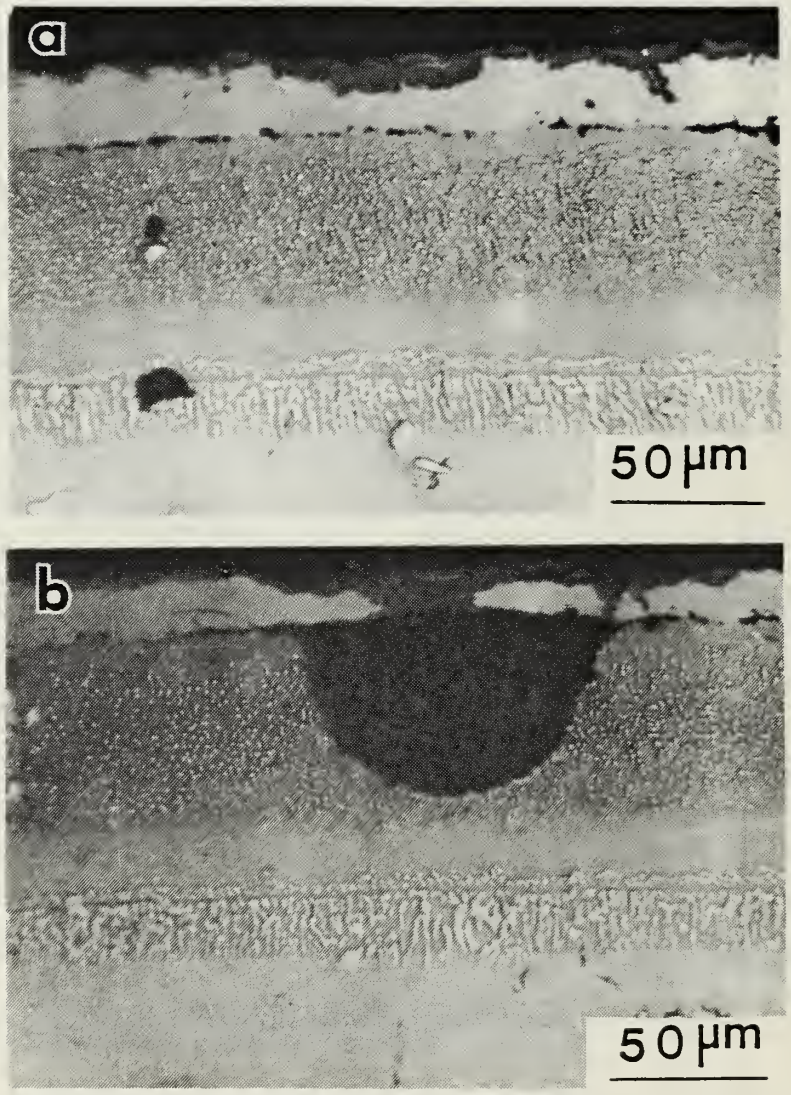

Figure 10. Typical low temperature hot corrosion attack at 700° C: (a) specimen exhibits little attack on $PtAl_2$ phase and (b) substantial hot corrosion attack beneath the $PtAl_2$ phase.

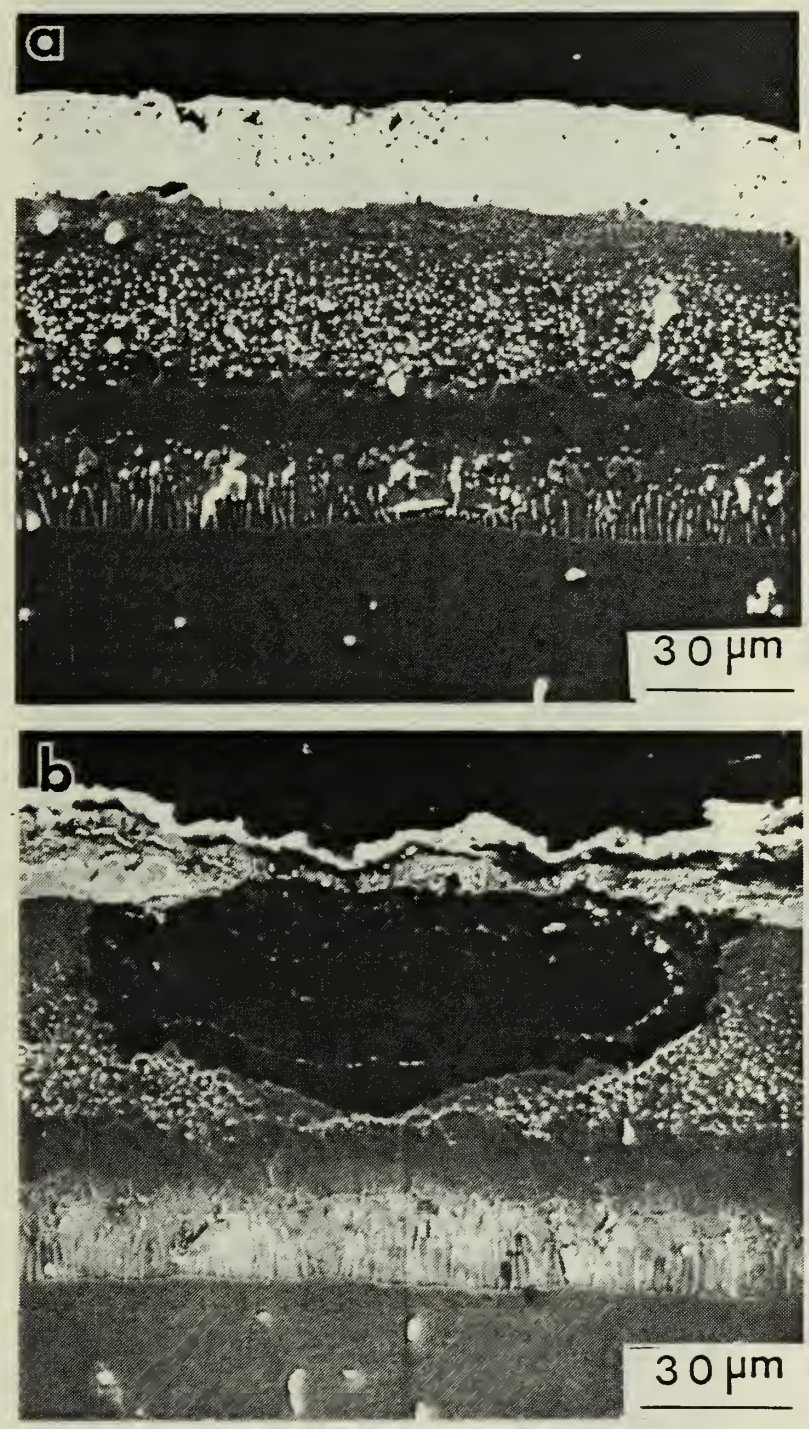

Figure 11. SEM photomicrographs exhibit: (a) inward type LTHA platinum-aluminide coating and (b) typical LTHC attack after 100 hours exposure at 700° C.

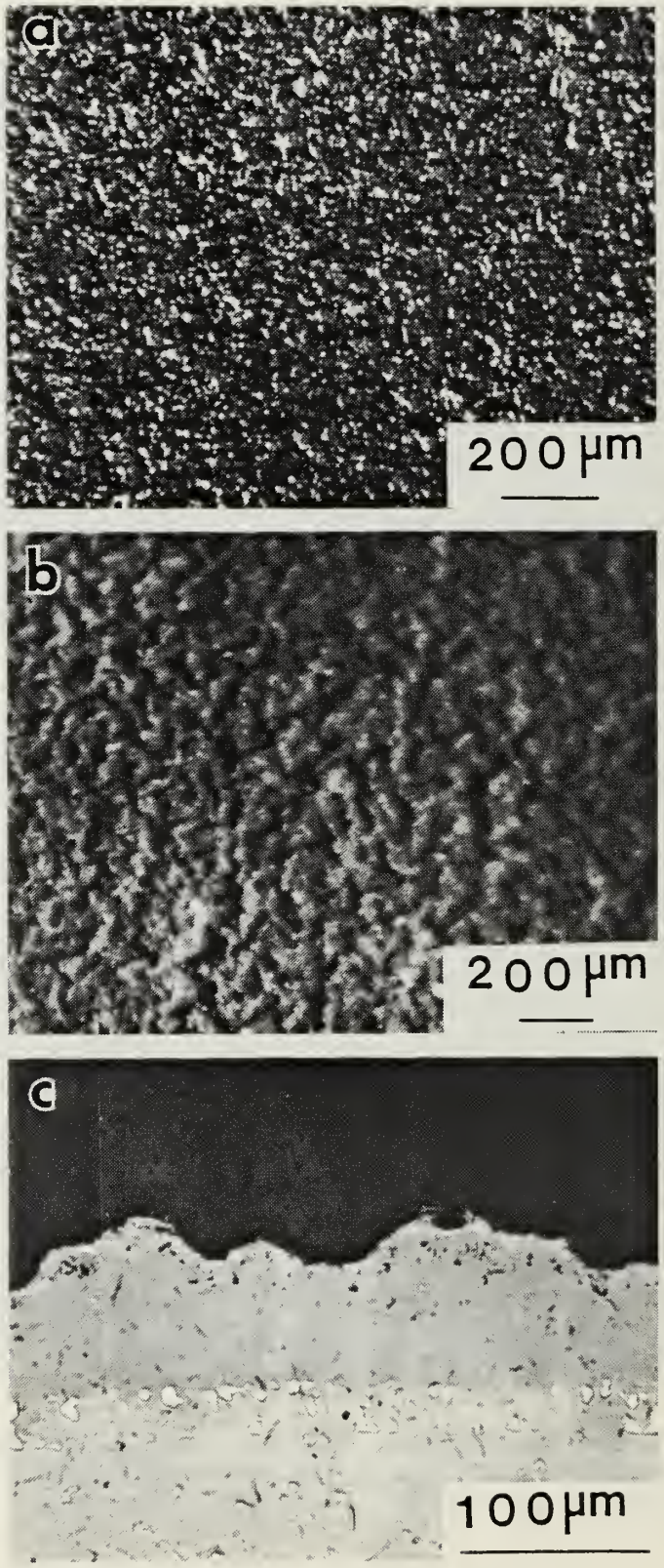

Figure 12. Typical example of surface rumpling of Pt-Al coatings: (a) sample exhibits macro surface roughness (8x), (b) enlarged photomicrograph (64x) and (c) cross-section of same specimen showing surface upheaval on the order of 50 um.

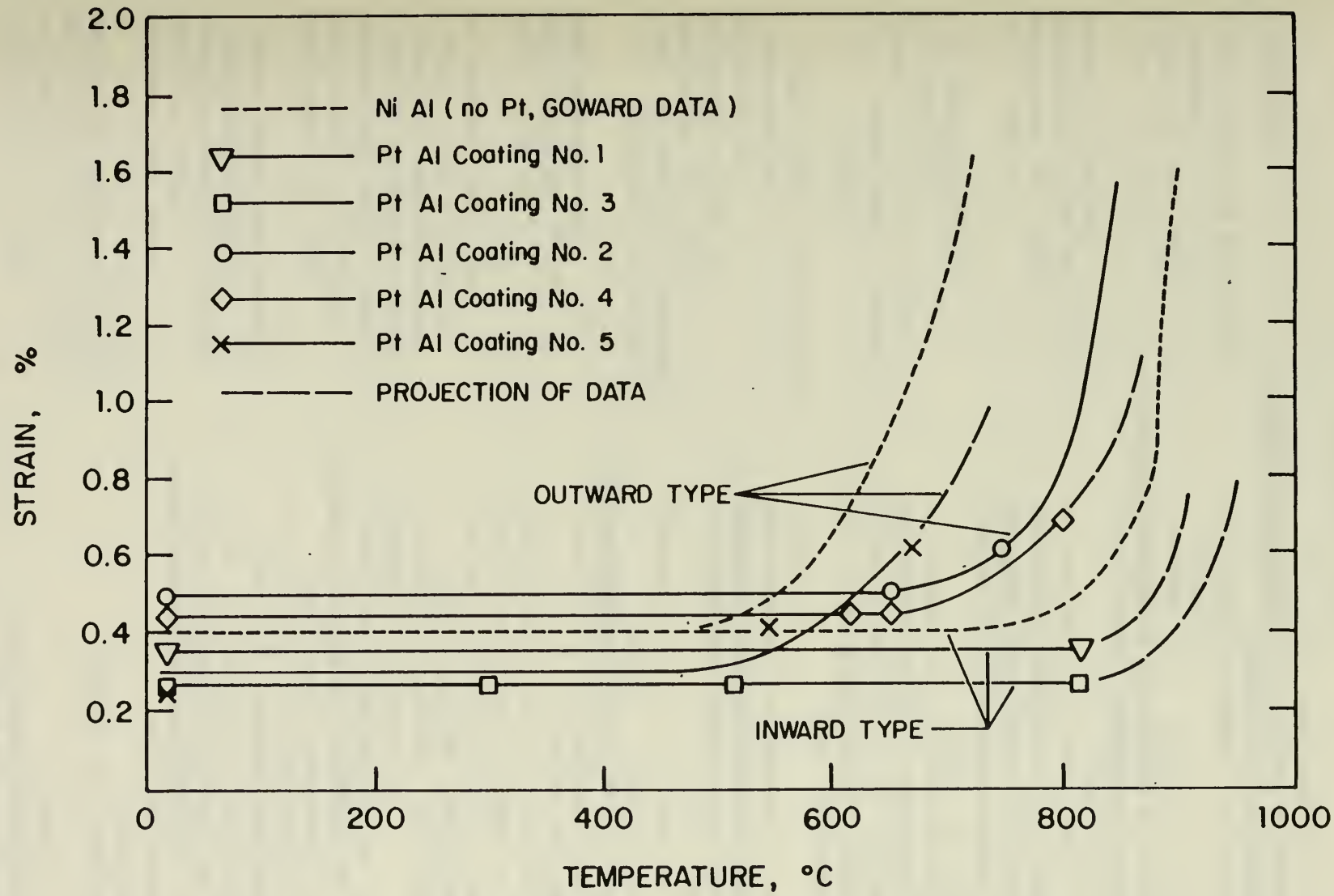

Figure 13. Ductile to brittle transition temperature (DBTT) and fracture strain of Pt-Al coatings as function of structure and Al-Pt content.

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